



Effect of the SiO₂ support on the catalytic performance of Ag/ZrO₂/SiO₂ catalysts for the single-bed production of butadiene from ethanol

Vanessa Lebarbier Dagle^{a,*}, Matthew D. Flake^a, Teresa L. Lemmon^a, Johnny Saavedra Lopez^a, Libor Kovarik^b, Robert A. Dagle^{a,*}

^a Institute for Integrated Catalysis, Pacific Northwest National Laboratory, 902 Battelle Blvd., Richland WA, 99354, USA

^b Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99354, USA

ARTICLE INFO

Keywords:

Ethanol
Butadiene
Biomass
Single-Step
SiO₂Ag/ZrO₂/SiO₂ acidity
Regeneration

ABSTRACT

A ternary Ag/ZrO₂/SiO₂ catalyst system was studied for single-step conversion of ethanol to butadiene by varying the catalyst composition (Ag, Ir, or Pt metal component, Ag/ZrO₂ loading, and choice of SiO₂ support) and operating conditions (space velocity and feed gas composition). Exceptional catalytic performance was achieved over a 1%Ag/4%ZrO₂/SiO₂-SBA-16 catalyst leading to 99% conversion and 71% butadiene selectivity while operating under mild conditions (325 °C, 1 atm, and 0.23 h⁻¹). Several classes of silica—silica gels, fumed silicas, mesoporous silicas—were evaluated as catalyst supports, and SBA-16 was found to be the most promising choice. The SiO₂ support was found to significantly influence both conversion and selectivity. A higher SiO₂ catalyst surface area facilitates increased Ag dispersion which leads to greater conversion due to the accelerated initial ethanol dehydrogenation reaction step. By independently varying Ag and ZrO₂ loading, Ag was found to be the main component that affects ethanol conversion. ZrO₂ loading and thus Lewis acid sites concentration was found to have little impact on the ethanol conversion. Butadiene selectivity depends on the concentration of Lewis acid site, which in turn differs depending on the choice of SiO₂ support material. We observed a direct relationship between butadiene selectivity and concentration of Lewis acid sites. Butadiene selectivity decreases as the concentration of Lewis acid sites increases, which corresponds to an increase in ethanol dehydration to ethylene and diethyl ether. Additionally, adding H₂ to the feed had little effect on conversion while improving catalytic stability; however, selectivity to butadiene decreased. Finally, catalyst regenerability was successfully demonstrated for several cycles.

1. Introduction

With an annual production of 11 million tons/year, butadiene is the most important conjugated diene, being the basis of a wide variety of synthetic rubbers, elastomers, and polymer resins upon polymerization by itself or in conjunction with other polymerizable monomers [1]. Currently, butadiene is primarily obtained as a byproduct of the ethylene production by steam cracking. The amount of butadiene produced from a steam cracker depends on the composition of the cracking feedstock used [2]. Heavier feedstocks such as naphtha produce more butadiene than lighter feedstocks such as ethane [2]. For example, an ethane steam cracker typically produces ~2 lb of butadiene per 100 lb of ethylene, while a naphtha steam cracker produces ~16 lb of butadiene per 100 lb of ethylene [3]. Currently, ethane is produced inexpensively from shale gas, which has become the preferred feedstock for steam cracking units in North America. Hence, butadiene co-

production has been in decline over the past decade. In addition to the shift in lighter feedstocks, crude oil price swings have historically led to corresponding price fluctuations in the cost of butadiene which is not ideal for end users. Thus, alternative technologies for producing butadiene are highly desired [4].

Ethanol-to-butadiene (ETB) represents an attractive alternative technology. Ethanol is commercially produced from renewable biomass or waste sources. In addition, the ethanol “blend wall” coupled with advancements in production efficiency and feedstock diversification will potentially lead to excess ethanol at competitive prices available for production of a wide range of fuels and commodity chemicals [5]. Furthermore, in recent publications, Patel et al. described an early-stage assessment method [6,7]. They compared the bioethanol-based pathway for butadiene production with the naphtha-based route and suggested that the bioethanol pathway could be a promising alternative to the naphtha-based process [6,7].

* Corresponding authors.

E-mail addresses: vanessa.dagle@pnnl.gov (V.L. Dagle), robert.dagle@pnnl.gov (R.A. Dagle).

Research on butadiene production was initiated in the early 20th century and numerous articles have since been published. One-step and two-step processes were developed in the former Soviet Union and the United States, respectively, for ethanol conversion to butadiene. A one-step catalytic process developed for ethanol conversion to butadiene was commercialized for some time to produce synthetic rubber but was abandoned later due to low-cost oil making more convenient the production of butadiene from petrochemical sources [8]. In principle, the one-step process offers greater simplicity and lower operating costs as compared to two-step processes. However, achieving high yields to butadiene at industrially relevant process conditions has been challenging. A large number of catalytic systems (e.g., doped Al_2O_3 , promoted MgO-SiO_2 , sepiolites, $\text{ZrO}_2\text{-Fe}_2\text{O}_3$, and zeolite-based catalysts) that are capable of converting ethanol to butadiene in one processing step have been reported [9–14]. These catalytic systems have been well summarized in recent reviews [1,4,8]. A number of studies have reported achieving 70 to 80% selectivity to butadiene. However, these results are usually obtained at low single-pass conversion (e.g., < 45%) or low catalyst space velocities (e.g., < 0.20 h^{-1}). For the single-step process to be commercially realized higher single pass conversions coupled with high selectivity ($\geq 70\%$) are likely required. Recently, several catalytic materials have distinguished themselves from others for their high catalytic performance. Using a $\text{Cu}_{1.0}\text{Hf}_{3.0}\text{Zn}_{0.5}/\text{SiO}_2$ catalyst operating at 360°C , weight hourly space volume (WHSV) = $0.21\text{ g}_{\text{EtOH}}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$ and atmospheric pressure, 72% butadiene selectivity at 99% conversion was obtained [15]. Under similar conditions (350°C , WHSV = $0.3\text{ g}_{\text{EtOH}}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$, $P = 1$ atmosphere), 75% butadiene selectivity of was obtained at 100% conversion for a 2% $\text{Zn}/8\%\text{Y}/\text{beta}$ catalyst. Ag/ZrO_2 catalysts supported on SiO_2 and Zeolite Beta also have shown very promising performance levels [14,16]. A 1% $\text{Ag}/10\%\text{ZrO}_2/\text{SiO}_2$ catalyst has been reported with catalytic performance achieving 74% butadiene selectivity and 88% conversion at 320°C , WHSV = $0.04\text{ g}_{\text{EtOH}}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$, and atmospheric pressure [17]. Under similar conditions and at low conversion a 1% $\text{Ag}/1\%\text{ZrO}_2\text{BEA}$ was found to be four times more active than a 1% $\text{Ag}/1\%\text{ZrO}_2/\text{SiO}_2$. However, commercialization of zeolite-based catalysts can be challenging because of the nature of chemicals used in the synthesis (e.g., hydrofluoric acid) and the waste produced (e.g. hydrochloric acid). In addition, pore confinement also can lead to increased catalyst deactivation by pore blocking and coking.

In this study, we have focused our understanding and further development of $\text{Ag}/\text{ZrO}_2/\text{SiO}_2$ catalysts for the ETB reaction. Although very encouraging results were obtained for the previously reported 1% $\text{Ag}/10\%\text{ZrO}_2/\text{SiO}_2$ catalyst [17], increasing catalytic activity while maintaining high selectivity to butadiene, thus enabling faster throughput, is highly desirable for commercial application. Therefore, we have further investigated the $\text{AgZrO}_2/\text{SiO}_2$ catalyst system with the goal of better understanding its structure-function relationship and improving yield to butadiene through improved catalyst design. We have studied the role that each individual component, Ag , ZrO_2 , and SiO_2 , has on the reaction mechanism. A supported Ag catalyst was compared to supported precious metal (i.e., Ir and Pt) catalysts. We comparatively evaluated several classes of silica supports studied how the nature of the SiO_2 support affects catalytic performance. We also evaluated catalyst lifetime and regenerability.

2. Experimental

2.1. Catalysts Synthesis

A series of $\text{xAg}/\text{yZrO}_2/\text{SiO}_2$ catalysts were synthesized by incipient wetness impregnation of SiO_2 with silver nitrate powder and zirconyl nitrate solution dissolved in deionized water. A total of 11 different SiO_2 materials were used as supports: 636, 645, 646, 923 (Davisil), silica gel large pores (alfa Aeser), silica gels KSKG-GOST 3956-76 and KSMG-GOST 3956-76 (JSC Karpov), mesoporous silicas SBA-15 and

SBA-16 (ACS Materials), fumed silica Aerosil 380 (Degussa) and L90 (Cab-O-Sil). After impregnation, the catalysts were dried at 110°C for 8 h and calcined at 500°C for 4 h. The Ag loading “x” was varied from 1 to 8 wt.% and the ZrO_2 loading “y” was varied from 1 to 10 wt.%. A bare SiO_2 was synthesized by impregnation of SiO_2 (Davisil 646) with deionized water and calcined under similar conditions as the other catalysts. A $4\text{ZrO}_2/\text{SiO}_2$ was prepared similarly to the $\text{xAg}/\text{yZrO}_2/\text{SiO}_2$ catalysts without addition of silver nitrate by impregnation of a silica gel 646 (Davisil). A 4 Ag/SiO_2 was prepared similarly to the $\text{xAg}/\text{yZrO}_2/\text{SiO}_2$ catalysts without addition of zirconyl nitrate solution by impregnation of a silica gel 646 (Davisil). A 11r/4 $\text{ZrO}_2/\text{SiO}_2$ catalyst, a 21r/4 $\text{ZrO}_2/\text{SiO}_2$ catalyst, and a 1 $\text{Pt}/4\text{ZrO}_2/\text{SiO}_2$ catalyst were prepared by incipient wetness impregnation of SiO_2 (Davisil 646) with zirconyl nitrate solution and Ir acetate solution (14 wt.%) or Pt nitrate solution (12 wt.%) dissolved in deionized water. The catalysts were dried at 110°C for 8 h and calcined at 500°C for 4 h. The supported Ir catalysts contain 1 wt.% and 2 wt.% of metal, while the supported Pt catalyst contains 1 wt.% metal. These three catalysts contain 4 wt.% ZrO_2 .

In the test, SiO_2 from Davisil was labeled $\text{SiO}_2\text{-x}$ where x stands for the Davisil number. The large-pore silica gel (alfa Aeser) was labeled $\text{SiO}_2\text{-AA}$. Silica gels KSKG-GOST 3956-76 and KSMG-GOST 3956-76, the mesoporous silica materials SBA-15 and SBA-16 (ACS Materials), and fumed silica Aerosil 380 (Degussa) and EL90 (Cab-O-Sil) were labeled $\text{SiO}_2\text{-KSKG}$, $\text{SiO}_2\text{-KSMG}$, $\text{SiO}_2\text{-SBA15}$, $\text{SiO}_2\text{-SBA16}$, $\text{SiO}_2\text{-A380}$ and $\text{SiO}_2\text{-EL90}$, respectively.

2.2. Catalyst characterization

2.2.1. BET

We used an automatic adsorptiometer (Micromeritics ASAP 2000) to measure nitrogen adsorption at 77 K. Samples were pretreated at 150°C for 12 h under vacuum. Surface areas were determined from adsorption values for five relative pressures (P/P_0) ranging from 0.05 to 0.2 using the Brunauer-Emmett-Teller (BET) surface method. The pore volumes were determined from the total amount of N_2 adsorbed between $P/P_0 = 0.05$ and $P/P_0 = 0.98$.

2.2.2. Pyridine adsorption/ desorption followed by infrared spectroscopy

We used a Nicolet FT-IR spectrometer IS50 equipped with a mercury cadmium telluride detector (resolution: 4 cm^{-1} , 128 scans) to record IR spectra. All spectra presented in this manuscript were normalized for 100 mg of the catalyst. Samples were pressed into pellets (ca. 20 mg for a 2-cm^2 pellet), and a pellet was placed inside the transmission IR cell. Samples were pretreated at 400°C under N_2 for 2 h and then under 10% H_2/N_2 at 325°C for 1 h before final cooling to 50°C . After pretreatment, pyridine was introduced at 50°C ($P_{\text{equilibrium}} = 133\text{ Pa}$), and the spectra were recorded following desorption from 50 to 350°C . The number of Lewis acid sites titrated by pyridine was calculated using an integrated molar absorption coefficient value of $\epsilon = 2.22\text{ cm}^2\text{ mol}^{-1}$ for ν_{19b} vibration of coordinated pyridine at ca. 1450 cm^{-1} [18].

2.2.3. X-ray powder diffraction

X-ray diffraction (XRD) spectra were recorded using a Philips X'pert MPD (Model PW3040/00) diffractometer with copper anode ($K\alpha_1 = 0.15405\text{ nm}$) and a scanning rate of 0.007° per second between $2\theta = 10^\circ$ to 70° . We used Jade 5 (Materials Data Inc., Livermore, CA) and the Powder Diffraction File database (International Center for Diffraction Data, Newtown Square, PA) to analyze diffraction patterns. The catalyst was reduced at 325°C for 1 h under 5% H_2/N_2 prior to XRD analysis.

2.2.4. Scanning transmission electron microscopy

Transmission electron microscopy (TEM) measurements were conducted with an FEI Titan 80–300 operated at 300 kV. All images were digitally recorded using a charge-coupled device (CCD) camera and were analyzed using Gatan Digital Micrograph. TEM images were

collected from at least five different locations on the grid. In general, TEM sample preparation involved mounting powder samples on copper grids covered with lacey carbon support films and then immediately loading them into the TEM airlock to minimize an exposure to atmospheric O₂. Before measurement, samples were reduced at 325 °C for 1 h under 10% H₂/N₂. Ag dispersion was calculated from the Ag⁰ particle size using the formula $D\% = 100/d$ where D represents the dispersion and *d* stands for the Ag⁰ particle size. A hundred particles were analyzed to determine the Ag⁰ particle size of each catalyst.

2.3. Reactivity measurements

Reactivity tests for the conversion of ethanol to butadiene were conducted in a 6.35-mm outer diameter (inner diameter = 4.57 mm) fixed-bed, packed-bed reactor loaded with 2.0 g of catalyst. A K-type thermocouple was placed in the reactor to measure the catalyst bed temperature. To minimize temperature gradients, an electrical resistance heating block was installed on the reactor. Prior to testing, catalysts were first activated in situ at 450 °C for 8 h under 120 SCCM of N₂. Then, the temperature was cooled to 325 °C, and the catalysts were reduced under 100 SCCM of 10% H₂/N₂ for 1 h. Ethanol fed into the system using an ISCO syringe pump was converted to the gas phase using a vaporizer consisting of 6.6-mm inner diameter steel tubing filled with quartz beads. The effects of conversion and selectivity were measured at 325 °C, atmospheric pressure, and varied WHSVs as noted. N₂ typically was used as the carrier gas. A knockout pot placed directly downstream of the reaction zone was used to collect liquid product. Gaseous effluent was analyzed online using an Inficon micro-GC (Model 3000 A) equipped with MS-5 A, Plot U, alumina, OV-1 columns, and a thermal conductivity detector. Liquid samples collected from the knockout pot were analyzed separately ex situ using liquid chromatography.

3. Results and discussion

3.1. Mechanistic considerations

The reaction mechanism for ETB has been studied extensively and many reaction mechanisms have been proposed [1,19–21]. The generally accepted reaction pathway involves the cascading sequence of reactions shown in Fig. 1 which includes dehydrogenation, condensation, and dehydration, occurring over a single multifunctional catalyst [1]. To verify the reaction pathway for Ag/ZrO₂/SiO₂ a space velocity study was conducted over the 4 Ag/4ZrO₂/SiO₂-646 catalyst. Fig. 2 shows the evolution of selectivity for butadiene, acetaldehyde, and crotonaldehyde as a function of the conversion. Other minor products were observed but not presented in Fig. 2 for simplification. These products include C₂-C₅ olefins, diethylether, acetone, butanol, ethyl acetate, CO₂, and smaller quantities of crotyl alcohol, methyl ethyl ketone and C₂-C₅ paraffins. As conversion increases from 7 to ~94%, butadiene selectivity increases from 0 to ~70%. Meanwhile, acetaldehyde selectivity decreases from 49 to 6% suggesting that acetaldehyde is an intermediate product involved in the formation of butadiene. While conversion increases from 7 to 50% selectivity toward crotonaldehyde increases from 0 to 1.5%, and decreases as conversion increases further. The selectivity curve for crotonaldehyde suggests that it is an intermediate product formed from acetaldehyde condensation. Hence, the observed relationship between butadiene and aldehyde selectivity with conversion supports the aldol condensation mechanism as presented in Fig. 1. This is also in agreement with results previously reported for a 1%Ag/4%ZrO₂/SiO₂ catalyst [17]. Here, an optimum butadiene yield of ~64% was obtained at ~94% conversion with a productivity of 0.14 g_{butadiene} produced/g_{cat}/h. A maximum butadiene productivity of approximately 0.9 g_{butadiene} produced/g_{cat}/h was reached at 50.2% conversion with a 20.2% butadiene yield.

In this study, we also investigated the effect of H₂ co-feed on the

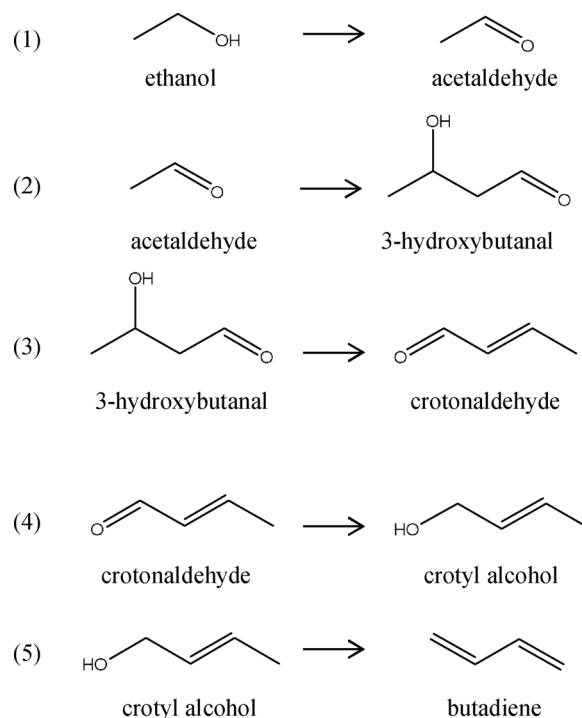


Fig. 1. Generally accepted reaction pathway for the formation of butadiene from ethanol. By-products are not included.

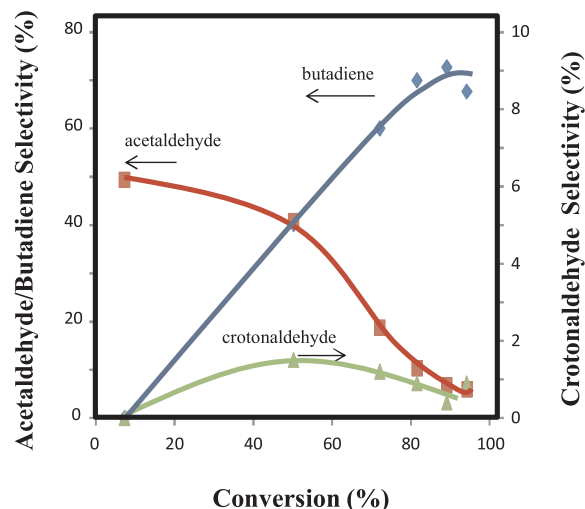


Fig. 2. Evolution of the selectivities to butadiene, acetaldehyde and crotonaldehyde as a function of the conversion over 4 Ag/4ZrO₂/SiO₂-646 catalyst. T = 325 °C, P = 1 atmosphere, WHSV = 0.37–38.0 h⁻¹, 50% ethanol/N₂.

activity and selectivity for supported Ag and Ir. In the presence of H₂ the olefins (e.g. butadiene, butenes) could be hydrogenated to alkanes. To our knowledge the impact that H₂ addition to the feed has on the mechanism and resulting catalytic performance has not been reported. Activity results presented in Table 1 for 4 Ag/4ZrO₂/SiO₂-646, 1Ir/4ZrO₂/SiO₂-646 and 2Ir/4ZrO₂/SiO₂-646 show only slight conversion changes after H₂ addition. Interestingly, for supported Ir catalysts, butadiene selectivity decreases drastically, and selectivity to butenes (i.e., 2-butene and 1-butene) increases significantly after addition of H₂ to the feed. For example, butadiene selectivity decreases from 60.4 to 0.7%, and selectivity to butenes increases from 11.0 to 53.0% over 2Ir/4ZrO₂/SiO₂-646. C₂-C₆ Alkanes selectivity increases also significantly likely due to complete hydrogenation of butadiene. This observed trend is not as pronounced over 4 Ag/4ZrO₂/SiO₂-646 as butadiene

Table 1Effect of H₂ addition to the feed on the catalytic performance over 4 A g/4ZrO₂/SiO₂-646, 1Ir/4ZrO₂/SiO₂-646 and 2Ir/4ZrO₂/SiO₂-646.

Catalyst	Gas feed composition (mol%) ^a	Conversion (%)	butadiene	C ₄ ⁼	C ₂ ⁼	C ₃ ⁼	C ₅ ⁼	C ₂ -C ₆ alkanes	butanol	crotonaldehyde	CH ₄	CO	Others ^{**}
4 A g/4ZrO ₂ /SiO ₂ -646	100%N ₂	91.6	68.3	6.4	8.8	1.6	0.8	0.3	1.2	0.5	0.0	0.0	12.1
4 A g/4ZrO ₂ /SiO ₂ -646	56.5%N ₂ /43.5%H ₂	87.7	63.2	10.8	11.2	1.7	0.4	0.4	0.8	0.5	0.0	0.0	11.0
1Ir/4ZrO ₂ /SiO ₂ -646	100%N ₂	92.3	65.7	8.7	2.0	2.4	0.9	0.8	1.9	1.1	1.7	3.0	11.8
1Ir/4ZrO ₂ /SiO ₂ -646	56.5%N ₂ /43.5%H ₂	96.0	3.6	53.0	1.5	4.9	1.9	9.8	1.4	1.4	5.2	5.1	11.2
2Ir/4ZrO ₂ /SiO ₂ -646	100%N ₂	95.8	60.4	11.0	2.1	2.6	1.8	1.3	1.9	1.2	2.6	4.0	11.3
2Ir/4ZrO ₂ /SiO ₂ -646	56.5%N ₂ /43.5%H ₂	97.5	0.7	44.5	0.8	5.7	2.8	15.3	1.2	1.6	7.5	9.0	10.9

^a feed is 24.3% ethanol in N₂/H₂ mixture.^{**} Others include: DEE, Ethyl acetate, acetaldehyde, acetic acid, butanone, pentanone, CH₄, CO, CO₂. T = 325 °C, P = 1 atmosphere, WHSV = 0.23 h⁻¹. SiO₂ = Davisil 646.

selectivity decreases only from 68.3 to 63.2% and selectivity to butenes increases from 6.4 to 10.8%. In addition, the C₂-C₆ alkanes selectivity is very similar (0.3% under N₂ vs. 0.4% under N₂ + H₂). The selectivity increase to butenes and alkanes observed for Ir catalysts as compared to Ag catalysts is indicative of a greater hydrogenation activity for Ir metal. Ag provides mild hydrogenation properties and this can explain in part why Ag/ZrO₂ catalysts are good candidates for the ETB process. Two reactions pathways have been proposed for the formation of butenes [1]. It was proposed that butenes could be produced from crotonaldehyde with a butanol intermediate and/or from crotyl alcohol with butanal and butanol intermediates. It also is possible that the presence of H₂ in the feed gas favors hydrogenation of butadiene to butenes. The butanol intermediate is likely produced via hydrogenation of crotonaldehyde, and one would expect crotonaldehyde selectivity to decrease with H₂ addition, if this pathway was responsible for the formation of butenes. However, as shown in Table 1, crotonaldehyde selectivity does not decrease when co-feeding H₂, indicating that butenes are not produced from crotonaldehyde. Isomerization of crotyl alcohol to butanal could be favored in the presence of H₂. However, the formation of butenes from crotyl alcohol via butanal and butanol intermediates cannot be verified because only trace amounts of these two compounds were detected. Separate experiments, not presented here, have shown an increase in selectivity to butenes and a corresponding decrease in butadiene selectivity with increasing contact time. Hence, we believe that butenes are, at least in part, produced from the hydrogenation of butadiene in the presence of H₂.

The role for each of the catalyst components (i.e., Ag, ZrO₂ and SiO₂) on the reaction steps was investigated by performing activity measurements under the same reaction conditions over 4ZrO₂/SiO₂-646, 4 A g/SiO₂-646, bare SiO₂-646, and 4 A g/4ZrO₂/SiO₂-646. The 4 A g/SiO₂-646 and 4 A g/4ZrO₂/SiO₂-646 catalysts present a similar conversion of ~88 to 89% as seen from Table 2. This result shows that ZrO₂, and thus the acid sites, have little impact on the ethanol conversion for supported Ag catalysts. This represents a significant finding because Lewis acid sites are known to be required for the ETB process, and ethanol conversion has previously been correlated with the concentration of Lewis acid sites for supported Ag/ZrO₂ catalysts [13,16]. Acetaldehyde is the primary compound produced over 4 A g/SiO₂-646 and SiO₂-646; however, the conversion is rather low at only 7% over

SiO₂-646. Similar results were obtained in a previous ETB study operated at 400 °C where low conversion (i.e., 6%) and high acetaldehyde selectivity (i.e., 51%) were obtained for SiO₂ [22]. In agreement with published results [11,23,24], these results indicate that Ag plays a major role in ethanol dehydrogenation to acetaldehyde. However, it does not imply that SiO₂ is not involved in acetaldehyde formation. Previous Fourier Transform Infrared Spectroscopy (FTIR) and kinetics experiments reported that the role of SiO₂ was to activate ethanol to yield a hydrogen-bonded surface complex which facilitates cleaving the O–H bond for the first step in ethanol dehydrogenation to acetaldehyde [25]. Both ZrO₂ and SiO₂ components contain acid sites that could be responsible for ethanol dehydration to ethylene and diethylether (DEE). However, only 2% yield toward ethylene and DEE was obtained for the bare SiO₂-646 as opposed to 14% yield for 4ZrO₂/SiO₂-646. Ethylene and DEE are thus mainly produced over the acid sites of ZrO₂ for 4ZrO₂/SiO₂-646 and 4 A g/4ZrO₂/SiO₂-646. According to Sushkevich et al. [24–26] for ZrO₂/SiO₂ catalysts, the acid sites of ZrO₂ also are responsible for the conversion of acetaldehyde to butadiene. Whereas for MgO/SiO₂ catalysts, acid sites of SiO₂ were proposed to be the active sites for the conversion of crotyl alcohol to butadiene [22]. In the present study, ZrO₂ acid sites appear to be responsible for the conversion of acetaldehyde into butadiene because butadiene selectivity increases from 0.9% for 4 A g/SiO₂-646 to 73.6% for 4 A g/4ZrO₂/SiO₂-646. In summary, these results show that Ag is mainly responsible for the conversion of ethanol to acetaldehyde, and ZrO₂ is required for conversion of acetaldehyde into butadiene. ZrO₂ also leads to the formation of undesired ethylene and DEE. To understand the role of the SiO₂ component we studied a series of Ag/ZrO₂ catalysts supported on different SiO₂ materials. The results are presented in the following section.

3.2. Influence of the SiO₂ support on catalytic performance

A few studies have reported how the SiO₂ support affects catalytic performance for the ETB reactions [22,27,28]. For one investigation of Ag/MgO catalysts supported on SiO₂ gel, mesoporous SiO₂, “COK-12,” and MCM-41, lower ethanol conversion was achieved with MCM-41 so it was found to be the least promising. The reason for this poor performance is inaccessibility to some of the Ag particles by the reactants

Table 2Reactivity performance for 4 A g/4ZrO₂/SiO₂-646, 4 A g/SiO₂-646, 4ZrO₂/SiO₂-646 and SiO₂-646.

catalyst	conversion (%)	Selectivities (%)						
		C ₂ ⁼	C ₄ ⁼	butadiene	acetaldehyde	Butyraldehyde	DEE	others
SiO ₂ -646	7.0	26.4	0	0	69.6	0	2.2	1.8
4ZrO ₂ /SiO ₂ -646	14.8	47.9	0.4	0	2.6	0	46.9	1.8
4 A g/SiO ₂ -646	88.3	1.5	5.9	0.9	61.4	12.9	0.1	17.3
4 A g/4ZrO ₂ /SiO ₂ -646	89.2	5.5	5.2	73.6	6.7	0	3.0	6.0

T = 325 °C, P = 1 atmosphere, WHSV = 0.47 h⁻¹, 50% ethanol/N₂. SiO₂ = Davisil 646. DEE = diethylether, others = butanol, MEK, crotonaldehyde, pentanone, acetone, ethyl acetate, acetic acid, C₃⁼, C₅⁼, C₂-C₅ alkanes and CO₂.

Table 3

BET Surface, pore volume, pores size, Lewis acid sites concentration, organic impurities contents for 1 A g/4ZrO₂/SiO₂ catalysts synthesized from different SiO₂ supports.

Support	BET surface (m ² /g)	Pore volume (ml/g)	Pore size- adsorption (Angstrom)	Lewis acid sites concentration ^a (umoles/g)	Organic impurities (ppm) ^{**}
SiO ₂ -636	442	0.84	80	32.2	Na:2200 K:270
SiO ₂ -AA	558	0.35	20 and 100	35.0	Na:2000 K:600
SiO ₂ -646	311	1.0	170	22.8	Na:2400 K:260
SiO ₂ -645	299	1.1	170	21.6	Na:500 K:1850
after K leaching				27.8	Na:300 K: 100
SiO ₂ -923	449	0.38	40	31.0	Na:2000 K:255
SiO ₂ -KSKG	381	0.67	75	26.1	Na:5500 K:350
					Mg:1100 Ca:3000
					Al = 3%
SiO ₂ -KSMG	475	0.26	20 and 40	NA	Na:5500 K:350
					Mg:1100 Ca:3000
					Al = 3%
SiO ₂ -EL90	91	1.6	> 200	NA	Na:2100 K:270
SiO ₂ -380	267	1.2	300	5.0	Na:2000 K:245
SiO ₂ -SBA15	728	1.1	75	NA	NA
SiO ₂ -SBA16	656	1.2	50 and 150	26.4	Na:100 K:730

^a Determined after pyridine adsorption at 50 °C and desorption at 150 °C.

^{**} determined by ICP.

[22]. An increase of butadiene selectivity as the pore size increased was reported for Zr:Zn supported on silica materials with different pore diameters [28]. For Ta/mesoporous SiO₂ (SBA-15, MCM-41, SiO₂ KIT-6), both pore size and the crystal size dimension of the SiO₂ was reported to control catalytic performance [27].

In the present study a series of 1 A g/4ZrO₂/SiO₂ catalysts were prepared from 11 different silica supports. A total of seven silica gels with different porosities and/or purity grades, two fumed silica materials, and two mesoporous silica materials (SBA-15 and SBA-16) were used as supports. The catalysts were characterized by N₂ adsorption, pyridine adsorption/desorption followed by FTIR spectroscopy and induced coupled plasma. An interesting finding from the results (see Table 3) is the large differences observed in resulting acidity, although the ZrO₂ loadings were similar. The Lewis acid site concentration is as low as 5 μmoles/g for the catalyst supported on SiO₂-380 and as high as 35 μmoles/g for the catalyst supported on SiO₂-AA.

All the catalysts were tested for ethanol conversion to butadiene under the same reaction conditions unless otherwise stated. As shown in Table 4, while the Ag and ZrO₂ loadings are the same for all the

catalysts, drastic differences in catalytic performance are achieved on the different silica supports. Indeed, the conversion varies from ~30% for the catalyst supported on SiO₂-645 (before ion-exchange) to ~100% conversion for the catalysts supported on SiO₂-KSMG and SiO₂-SBA-16. The selectivity of the products also varies greatly depending on the silica support used. For example, no butadiene was produced for the catalyst supported on SiO₂-KSMG, whereas 78.3% butadiene selectivity was obtained with the catalyst supported on SiO₂-KSKG. Compared to the other catalysts, acetaldehyde selectivity is high for 1 A g/4ZrO₂/SiO₂-380 (i.e., 42.5% acetaldehyde). This is likely due to the low concentration of Lewis acid sites (5 μmoles/g) because acid sites were found to promote acetaldehyde conversion to butadiene. High ethylene selectivity (48.7%) was observed for 1 A g/4ZrO₂/SiO₂-AA, and this performance level can be attributed to the high concentration of Lewis acid sites (35 μmoles/g) that promote ethanol dehydration to ethylene and DEE. These results show that there is an optimal amount of acid sites required to convert acetaldehyde into butadiene while minimizing ethanol dehydration.

In the present study both catalysts prepared from the SiO₂-645 and

Table 4

Effect of the SiO₂ support on the catalytic performance of 1 A g/4ZrO₂/SiO₂ catalysts.

Support	WHSV (h ⁻¹)	Conv (%)	Selectivities (%)										Butadiene yield (%)	Productivity ^c
			butadiene	C ₂ ⁼	C ₃ ⁼	C ₄ ⁼	DEE ^a	Ethyl acetate	butanol	acetaldehyde	crotonaldehyde	Others ^b		
SiO ₂ -636	0.23	82.7	65.2	7.3	1.9	14.1	2.5	1.2	1.2	3.8	0.2	2.6	51.4	0.07
SiO ₂ -AA	0.23	48.7	29.3	48.7	1.1	3.7	9.9	0.5	0.4	4.5	0.2	1.7	14.3	0.02
	0.11	81.3	36.7	41.4	1.6	2.3	7.7	0.3	0.4	2.8	0.0	6.8	29.8	0.02
SiO ₂ -646	0.23	76.1	75.3	3.3	1.4	4.9	1.6	2.1	1.9	5.9	0.3	3.3	57.3	0.08
SiO ₂ -645	0.23	29.5	41.6	15.9	1.2	3.7	4.7	0.6	3.8	12.4	0.5	15.6	12.3	0.02
after ion-exchange	0.07	82.0	75.1	3.4	1.8	6.5	1.6	1.8	1.6	3.4	0.8	4.0	61.6	0.03
	0.23	79.6	73.4	5.3	1.7	5.1	1.8	1.8	1.4	5.0	0.7	3.8	58.4	0.08
SiO ₂ -923	0.23	84.8	56.8	20.2	1.9	6.4	5.9	1.1	0.7	4.2	0.2	2.6	48.2	0.07
SiO ₂ -KSKG	0.23	84.7	78.3	1.8	1.5	4.2	0.7	1.0	2.2	5.9	0.8	3.6	66.3	0.09
SiO ₂ -KSMG	0.23	100.0	0.0	97.9	0.2	0.9	0.0	0.0	0.0	0.7	0.0	0.3	0	0
SiO ₂ -EL90	0.23	37.1	39.2	22.0	1.0	3.4	10.0	1.4	0.4	12.2	0.3	10.1	14.5	0.02
SiO ₂ -380	0.23	39.2	29.6	12.4	0.3	2.1	3.4	1.4	2.3	42.5	1.3	4.5	11.6	0.02
SiO ₂ -SBA15	0.23	97.8	46.6	29.4	2.3	10.5	7.0	0.1	0.5	1.6	0.4	1.6	45.6	0.06
SiO ₂ -SBA16	0.23	99.0	70.5	5.8	2.8	11.2	2.6	0.3	0.9	1.5	0.7	3.7	69.8	0.09

T = 325 °C, P = 1 atmosphere, 24.3% ethanol in N₂.

^a DEE = Diethylether.

^b Others include: acetic acid, butanone, pentanone, C₂-C₅ alkanes, C₅⁼, CO₂, CH₄ and CO.

^c productivity = gram of butadiene produced per gram catalyst and per hour.

SiO₂-646 present similar BET surfaces, pore volumes, pore sizes, and acid site concentrations. However, when tested under the same reaction conditions, conversion and butadiene selectivity are significantly higher for the 1 A g/4ZrO₂/SiO₂-646. Indeed, the conversion and butadiene selectivity for these catalysts are equal to 76.1% and 75.3%, respectively, for 1 A g/4ZrO₂/SiO₂-646 and equal to 29.5% and 41.6%, respectively, for 1 A g/4ZrO₂/SiO₂-645. The catalysts synthesized from SiO₂-645 have a high K content (i.e., 1850 ppm) compared to the one synthesized from SiO₂-646 (i.e. 260 ppm). It is possible that the K impurity impedes ethanol conversion. To test this hypothesis, aqueous NH₄OH was used to leach K from the SiO₂-645. As shown in Table 3, the K concentration was reduced to ~100 ppm after leaching. After leaching K, the 1 A g/4ZrO₂/SiO₂-645 achieved a conversion of 79.6% and a selectivity to butadiene of 73.4%, which is similar to the results obtained for the 1 A g/4ZrO₂/SiO₂-646 catalysts. Hence, these results suggest that the K impurity inhibits ethanol conversion.

Among all the catalysts tested, 1 A g/4ZrO₂/SiO₂-SBA16 is the most active toward butadiene formation, exhibiting a butadiene yield of 70%. Performance of the 1 A g/4ZrO₂/SiO₂-SBA16 catalyst was compared under similar space velocities and temperatures with what we believe are among the most active catalysts recently presented in the literature and under similar space velocities and temperatures. The results are summarized in Table 5. The comparison of Ag/ZrO₂/SiO₂-SBA16 catalysts shows that a butadiene yield above 60% was obtained in the present study as opposed to only 39% previously reported for a 2 A g/4ZrO₂/SiO₂ catalyst. Also, among all the catalysts presented in Table 5, 2%Zn8%Y/Beta presents the highest butadiene yield of 75%, as compared to approximately 70% for this work. At same space velocity (i.e., WHSV = 0.2–0.3 h⁻¹) 2%Zn8%Y/Beta also shows the highest productivity of 0.12 g_{butadiene} /g_{cat}/h. However, ZnY/Beta catalysts seem to suffer from rapid deactivation as compared to the Ag/ZrO₂/SiO₂-SBA16 catalyst. Indeed, for a 5%Zn5%Y/Beta catalyst a decrease of conversion from ~90% after 1 h of reaction to ~76% after 7 h of reaction was observed [29]. Here, as shown in Fig. 8, 1 A g/4ZrO₂/SiO₂-SBA16 shows a lower decrease in conversion from only 99% (TOS = 1 h) to 96% (TOS = 5 h). In addition, butadiene selectivity remains stable with time on stream, whereas a decrease of butadiene selectivity from about 72% to 62% was observed for the 5%Zn5%Y/Beta catalyst.

Our study clearly demonstrates the strong influence the SiO₂ support has on the catalytic performance of Ag/ZrO₂/SiO₂ catalysts for butadiene production from ethanol. From this work, it is observed that any Ag/ZrO₂/SiO₂ catalyst formulation is not necessarily active for the ETB process, and butadiene production is dependent of the choice of material used for the SiO₂ support. We decided to investigate further the effect of SiO₂ on both conversion level and butadiene selectivity. Regarding the conversion level, we showed in the previous section that ZrO₂ does not have a significant impact on ETB conversion and Ag is the main component responsible for ethanol conversion to acetaldehyde. As shown in Fig. 3(a) ETB conversion generally increases as the catalyst

surface area increases suggesting that the ETB conversion increase is due to better dispersion of Ag with the increase of the SiO₂ support surface area. To verify this hypothesis, the Ag particle size was measured by TEM after reduction for the majority of the catalysts to determine Ag dispersion. The results are presented Fig. 3(b). The general trend shows that catalysts with lower conversion between 29 and 40% present lower Ag dispersion equal to ~20%, whereas conversion of ~80% is obtained for catalysts with higher Ag dispersions between 30 and 50%. The 1 A g/4ZrO₂/SiO₂-SBA16 catalyst with the highest conversion (i.e., 99%) presents the highest Ag dispersion. For this catalyst, TEM images exhibit the presence of ~1 nm particles and also smaller Ag clusters. Note that a 1-nm particle is equivalent to 100% dispersion using the general formula $D(\%) = 100/d$ (D = dispersion; d = particle size). Thus, we can assume 100% dispersion for the 1 A g/4ZrO₂/SiO₂-SBA16 catalyst for comparison with the other catalysts. The results suggest that the increase of ethanol conversion is due to an increase of the Ag dispersion. Hence, the surface area of the SiO₂ support is a major parameter affecting ETB conversion.

We have also examined how the SiO₂ support affects butadiene formation. Acid sites are responsible for the conversion of acetaldehyde to butadiene. SiO₂ alone is not responsible for the catalyst acidity. As shown in Table 2, the bare SiO₂ produces mainly acetaldehyde from ethanol, and ZrO₂ is required to produce butadiene. Hence, it is believed that the interaction between ZrO₂ and SiO₂ varies greatly depending of the SiO₂ support which ultimately affects catalyst acidity and butadiene selectivity. The XRD pattern recorded for 1 A g/4ZrO₂/SiO₂-636, which is characteristic of patterns obtained for other samples with 1% Ag is presented Fig. 4. No peaks characteristic of crystalline ZrO₂ are observed suggesting that Zr is not present as crystallized ZrO₂. Also, it does not exhibit the presence of Ag (peaks at $2\theta = 38.1^\circ$ and 44.3°) indicating that the size of the Ag particles are < 4 nm. TEM images obtained for 1 A g/4ZrO₂/SiO₂-636 and presented in Fig. 5 do not suggest that Zr is present as crystalline ZrO₂ because no facets are seen. The images show ZrO_x patches widely dispersed on the SiO₂. It is believed that these ZrO_x patches interact with the SiO₂ support to modify the acidity of the catalyst. Depending on the SiO₂ support the interaction between the ZrO_x patches and SiO₂ could differ and affect the catalyst acidity.

3.3. Influence of the catalyst composition on catalytic performance

Previously it was demonstrated that both Ni and Cu are less active than Ag for ETB over 0.3%Metal/4ZrO₂/SiO₂ [17]. In the present study, we have compared the performance of the non-precious supported Ag catalyst with the one for supported precious Ir and Pt metals. Because of its high selectivity toward dehydrogenation, Pt is often used in dehydrogenation reaction [30]. Ir was selected in an attempt to make finely dispersed particles leading to high dispersion and thus high conversion. This approach is based on previous work from our group where for supported Ir catalysts, single Ir atoms and Ir particles that were ≤ 2 nm

Table 5

Catalytic performance comparison between this work and the best performing catalysts from the literature under similar reaction conditions (T = 320–350 °C, WHSV = 0.2–0.5 h⁻¹, P = 1 atmosphere).

catalyst	Temperature (°C)	WHSV (h ⁻¹)	Conversion (%)	Butadiene selectivity (%)	Butadiene yield (%)	Productivity***	Ref.
1 A g/4ZrO ₂ /SiO ₂ -SBA16*	325	0.23	99.0	70.5	69.8	0.09	This work
4 A g/4ZrO ₂ /SiO ₂ -646**	325	0.47	89.2	73.6	61.5	0.17	This work
2 A g/4ZrO ₂ /SiO ₂ **	320	0.3	55.2	71.3	39.4	0.07	[17]
2%Zn-8%Y/beta	330	0.3	90	81.0	72.9	0.11	[29]
	350		100	75.0	75.0	0.12	
Cu _{1.0} Hf _{3.0} Zn _{0.5}	360	0.21	99	72.0	71.6	0.09	[15]

* T = 325 °C, P = 1 atmosphere, 24.3% ethanol/N₂.

** T = 325 °C, P = 1 atmosphere, 50% Ethanol/N₂.

*** Productivity = grams of butadiene per gram of catalyst and per hour.

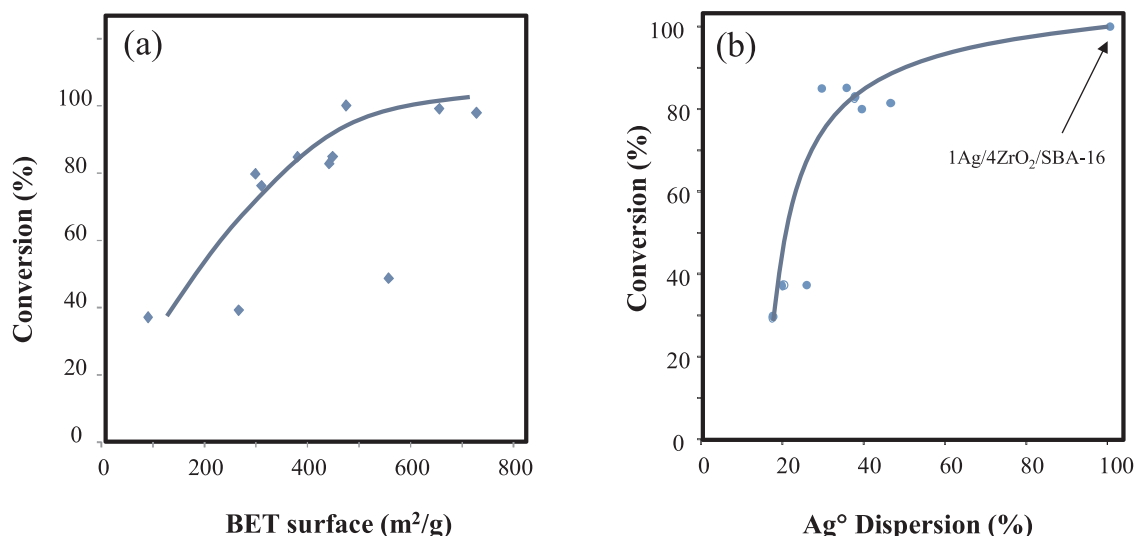


Fig. 3. Evolution of the conversion with (a) the BET surface and (b) the Ag° dispersion for 1 Ag/4ZrO₂/SiO₂ catalysts prepared from different silicas. The dispersion was measured via TEM after reduction. T = 325 °C, WHSV = 0.23 h⁻¹, P = 1 atmosphere, 24.3% ethanol in N₂.

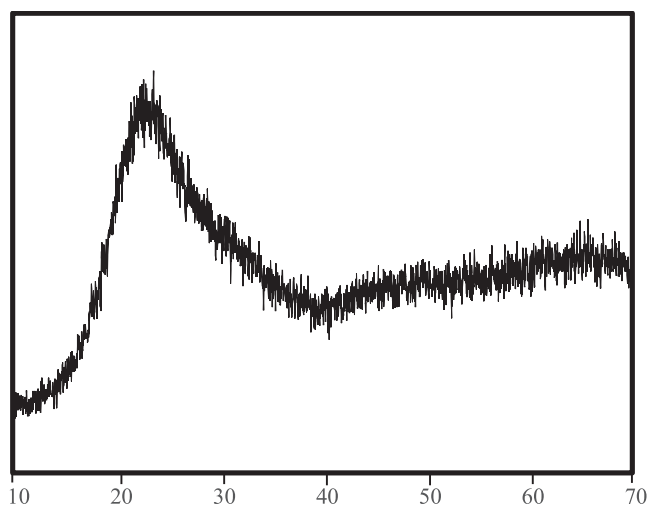


Fig. 4. XRD pattern for 1 Ag/4ZrO₂/SiO₂-636 recorded between 2 θ = 10–70° after reduction at 325 °C for 1 h under 10% H₂/N₂.

in size were observed [31–33]. The catalytic performance of the 1 Ag/4ZrO₂/SiO₂-646 catalyst was thus compared when promoting with either Pt or Ir versus Ag. As reported in Table 6, under the same reaction conditions, the activity is highest for the supported Pt catalyst because full conversion was achieved. It is the lowest for the supported Ag catalyst with a conversion of 47.9%. While the 1 Pt/4ZrO₂/SiO₂-646 catalyst is the most active for ethanol conversion, the selectivity to butadiene is very low and equal to 4% and the main products appears to be undesired CH₄ and CO. Thus, Pt metal is not the metal of choice for ETB. Interestingly, the 1 Ir/4ZrO₂/SiO₂-646 catalyst presents not only higher conversion (85.4%) than the supported Ag catalyst but also a higher butadiene selectivity (62.8%). Hence, under similar reaction conditions higher butadiene production was achieved using the supported Ir metal catalyst. To determine which of the catalysts is the most selective to butadiene a selectivity comparison was made at similar conversion (76 to 86%). One can see from Table 6 that the highest selectivity toward butadiene (75.3%) was achieved with the 1 Ag/4ZrO₂/SiO₂-646 catalyst. The least selective catalyst was still 1 Pt/4ZrO₂/SiO₂-646 for which selectivity to butadiene is negligible. For ZrO₂/SiO₂ catalysts the Ag metal is preferred over Ir and Pt to produce butadiene from ethanol. We have thus examined the effect of Ag

loading on the reactivity.

In a previous study, for Ag/ZrO₂/SiO₂ catalysts with Ag loadings between 0.3% and 2% [17], the increase of conversion was found to be marginal for Ag > 1% (i.e., conversion = 48% for 1% Ag and conversion = 55% for 2% Ag). Here, we investigated the effect of Ag loading between 1 and 8% (Table 7). The conversion increases significantly from 71 to 90.5% when the Ag loading increases from 1 to 4%, and for Ag > 4%, the conversion increases slightly to 92.4%. Hence, by studying a broad range of Ag loadings, one can see that an Ag loading above 1% is beneficial to enhance activity. In agreement with previous results obtained over Ag/MgO/SiO₂ catalysts [22] an increase in acetaldehyde selectivity from 5.7 to 7.7% and a decrease of butadiene selectivity from 71.3 to 66.3% is observed when the Ag loading increases from 1 to 8%. It is likely that increasing the Ag content leads to an increase of the number of Ag particles active for ethanol dehydrogenation to acetaldehyde, leading to an increased amount of acetaldehyde that is not readily converted into butadiene. At similar conversion (~89% to 82%) butadiene selectivity ranges from ~66 to 67% for all three catalysts. Due to the increased amount of Ag particles active for ethanol dehydrogenation, acetaldehyde selectivity increases from 3 to 7.7% when the Ag loading increases from 1 to 8%. Overall, 4 Ag/4ZrO₂/SiO₂-636 is more active than 1 Ag/4ZrO₂/SiO₂-636. The catalysts with 4 and 8% Ag present similar activity and selectivity.

The effect of ZrO₂ loading between 1 and 10 wt. % was examined for a 4 Ag/yZrO₂/SiO₂-646 catalyst. The conversion reported in Table 8 is insignificantly affected by the ZrO₂ loading. Indeed, while the ZrO₂ loading quadruple from 1 to 4% the conversion increases only slightly from ~79% to ~86%. Above 4% ZrO₂ loading the conversion decreases (i.e. 82.3% for 10% ZrO₂ loading). Those results are in agreement with those reported in Table 2 showing that adding 4% ZrO₂ to 4 Ag/SiO₂ did not lead to a significant increase of conversion. Suskevich et al. have found an increase of ethanol conversion from 18 to 48% while the ZrO₂ content increases from 1 to 4% for Ag/ZrO₂/SiO₂ catalysts. However, in agreement with our study, a further increase of ZrO₂ loading from 4 to 18% did not affect significantly the conversion equal to 45–48% [17]. Butadiene selectivity decreases from ~71 to ~62% when the ZrO₂ loading increases from 1 to 10%. Similarly, acetaldehyde selectivity decreases from ~14% to ~9%. On the contrary, ethylene and DEE selectivity both increase with the ZrO₂ loading, from ~4 to 8% and ~1 to 2.5%, respectively. This is to be expected because increasing the ZrO₂ loading leads to an increase in the concentration of the Lewis acid sites (see Table 8), and ethanol dehydration to ethylene and DEE is catalyzed by acid sites. Surprisingly, in their work

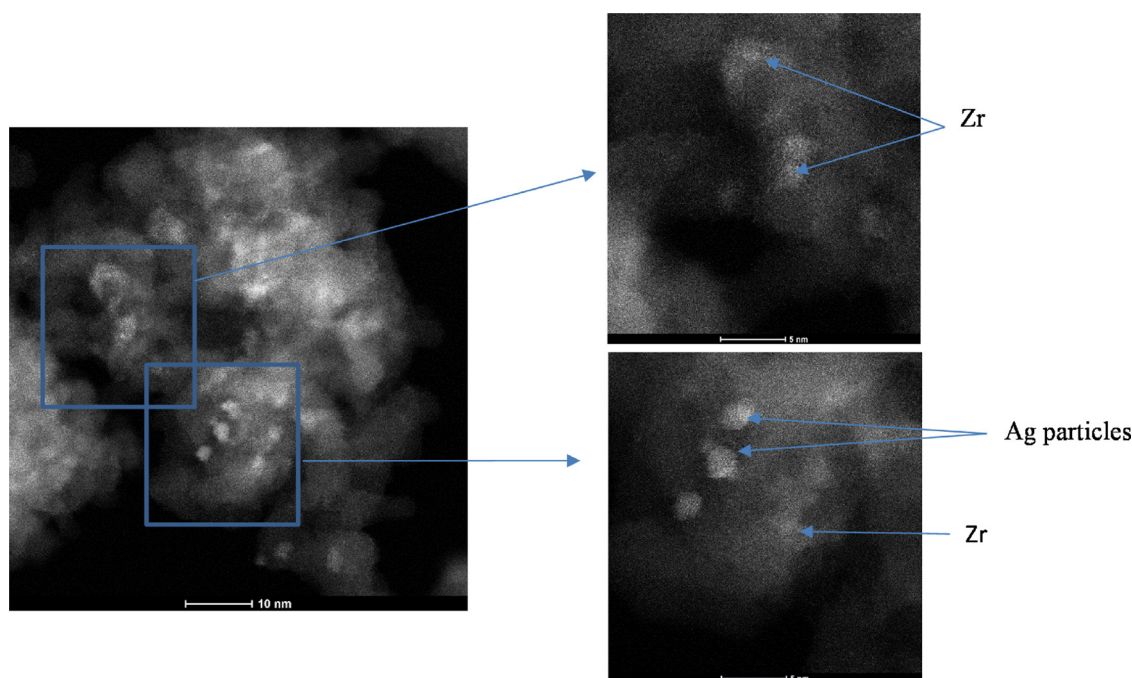


Fig. 5. TEM images for 1 Ag/4ZrO₂/SiO₂-636 recorded after reduction at 325 °C for 1 h under 10% H₂/N₂.

Table 6

Effect of the nature of the metal Ag, Pt or Ir on the catalytic performance.

Catalyst	Conversion (%)	Selectivities (%)												
		butadiene	C ₂ ⁼	C ₃ ⁼	C ₄ ⁼	DEE [*]	Ethyl acetate	butanol	acetaldehyde	crotonaldehyde	CH ₄	CO	CO ₂	Others ^{**}
1 Ag/4ZrO ₂ /SiO ₂ -646	47.9	57.7	13.9	1.1	5.9	5.0	0.6	1.5	10.0	0.2	0	0	0.4	3.7
1 Ir/4ZrO ₂ /SiO ₂ -646	85.4	62.8	2.0	1.8	9.9	0.6	1.7	2.0	8.9	2.2	1.3	2.2	0.3	4.2
1 Pt/4ZrO ₂ /SiO ₂ -646	100	4.0	0.0	0.0	0.4	0.8	0.4	0.0	0.0	0.0	31.2	22.9	14.4	25.9
T = 325 °C, P = 1 atmosphere, WHSV = 0.34 h ⁻¹ , 24.3% ethanol/N ₂ .														
1 Ag/4ZrO ₂ /SiO ₂ -646	76.1	75.3	3.3	1.4	4.9	1.6	2.1	1.9	5.9	0.3	0	0	0.4	2.9
1 Ir/4ZrO ₂ /SiO ₂ -646	85.4	62.8	2.0	1.8	9.9	0.6	1.7	2.0	8.9	2.2	1.3	2.2	0.3	4.2
1 Pt/4ZrO ₂ /SiO ₂ -646	86.4	0.0	2.1	5.2	0.6	0.1	3.1	0.3	23.6	0.2	24.4	32.5	0.2	7.7
T = 325 °C, P = 1 atmosphere, WHSV varied between 0.23–18.1 h ⁻¹ , 24.3% ethanol/N ₂ .														

* DEE = Diethylether.

** others include C₂–C₅ alkanes, C₅ olefins, butanone, pentanone, acetic acid. SiO₂ = Davisil 646.

Sushkevich et al. did not find an increase in ethylene or DEE selectivity when the ZrO₂ loading increases [17]. Selectivity of both ethylene and DEE are low in their study (between 2 and 3%), and it is possible that uncertainty regarding the measurements is high for this level of selectivity and might mask any trend. Among all 4 Ag/ZrO₂ catalysts supported on the Davisil 646 silica gel, 4 Ag/4ZrO₂/SiO₂-646 presents the highest yield toward butadiene (59.4%).

3.4. Evidence of a direct relationship between lewis acid site concentration and butadiene selectivity

As explained above, acid sites play a major role in the conversion of acetaldehyde to butadiene. Many studies have reported on the importance of the acidity for ETB [15,17,22,34]. It is generally reported that Lewis acid sites are active for the MPV reduction of crotonaldehyde and for the aldol condensation of acetaldehyde [15,22,26,35]. It is unclear whether the acidity affects ethanol conversion and/or the product

Table 7

Effect of the Ag loading on the catalytic performance of xAg/4ZrO₂/SiO₂-636 catalysts.

Ag loading (wt %)	WHSV (h ⁻¹)	Conversion (%)	Selectivities (%)									
			butadiene	C ₂ ⁼	C ₃ ⁼	C ₄ ⁼	DEE [*]	Ethyl acetate	butanol	acetaldehyde	crotonaldehyde	Others ^{**}
1	0.18	89.1	66.3	14.1	1.9	6.2	5.4	0.7	0.7	3.0	0.2	1.5
1	0.45	71.0	71.3	8.4	1.5	4.9	2.8	1.2	1.4	5.7	0.2	2.6
4	0.45	90.5	67.2	10.5	1.5	5.6	3.5	1.3	0.9	6.6	0.5	2.4
8	0.45	92.4	66.3	9.5	1.5	6.6	2.2	1.1	1.0	7.7	0.8	3.3

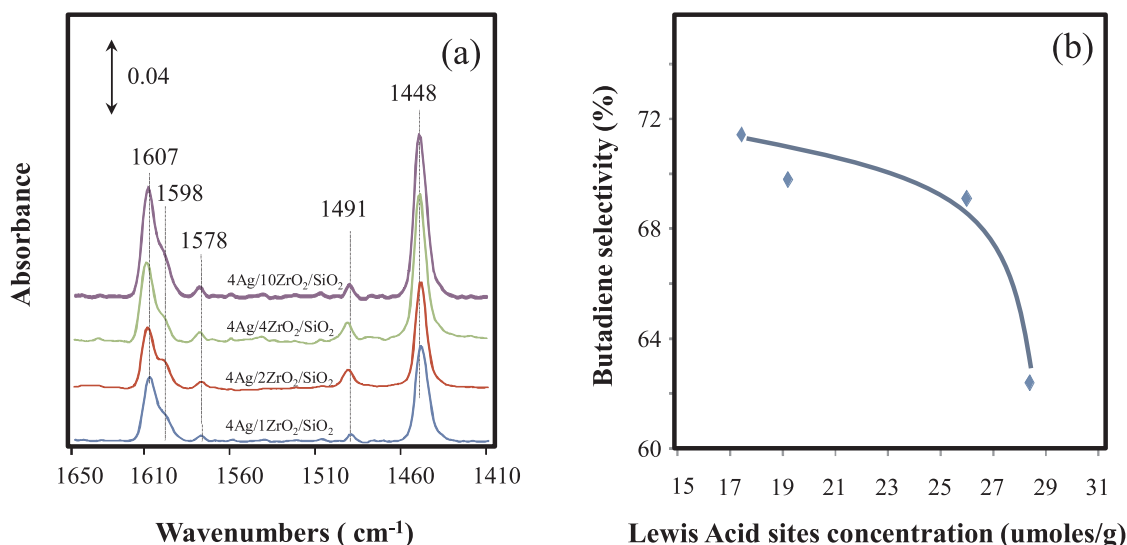
T = 325 °C, P = 1 atmosphere, 24.3% ethanol in N₂, SiO₂ = Davisil 636.

* DEE = Diethylether.

** others = C₅ olefins, C₂–C₅ alkanes, acetic acid, acetone, butanone, pentanone, CO₂.

Table 8Effect of the ZrO₂ loading on the catalytic performance for 4 Ag/yZrO₂/SiO₂-646 catalysts and Lewis acid sites concentration.

ZrO ₂ loading (wt %)	Lewis acid sites concentration (umoles/g)	Conversion (%)	Selectivities (%)									
			butadiene	C ₂ =	C ₃ =	C ₄ =	DEE [*]	Ethyl acetate	butanol	acetaldehyde	crotonaldehyde	Others ^{**}
1	17.3	78.6	71.2	4.1	1.0	2.4	1.3	1.4	0.8	14.2	1.1	2.5
2	19.2	80.6	69.8	5.1	1.0	4.1	2.1	2.1	1.4	10.7	0.9	2.8
4	26.0	85.9	69.1	3.7	1.2	5.5	1.6	2.9	1.8	9.2	0.7	4.3
10	28.4	82.3	62.4	8.4	1.3	5.7	2.5	3.1	1.7	9.3	0.8	4.8

T = 325 °C, WHSV = 0.45 h⁻¹, P = 1 atmosphere, 24.3% ethanol in N₂, SiO₂ = Davisil 646.^{*} DEE = Diethylether.^{**} others = C₅ olefins, C₂-C₅ alkanes, acetic acid, acetone, butanone, pentanone, CO₂. Acid sites determined after pyridine desorption at 150 °C.**Fig. 6.** (a) Infrared spectra recorded after pyridine adsorption at 50 °C followed by desorption at 150 °C for 4 Ag/yZrO₂/SiO₂-646 catalysts. Spectra were normalized to a pellet of 20 mg and 2 cm². (b) Evolution of the butadiene selectivity with the concentration of Lewis acid sites determined after pyridine desorption at 150 °C.

selectivity. In addition, the relationship between the concentration of acid sites and butadiene selectivity remains unclear. In this study, catalyst acidity was investigated by pyridine adsorption/desorption followed by infrared spectroscopy to determine the nature and the concentration of the acid sites. Fig. 6(a) shows the normalized infrared spectra recorded after pyridine adsorption at 50 °C followed by desorption at 150 °C between 1410 and 1650 cm⁻¹ for the 4 Ag/yZrO₂/SiO₂-646 with ZrO₂ loading between 1 and 10 wt.%. Bands located at 1607, 1578, 1448, and 1491 cm⁻¹ and a shoulder at 1598 cm⁻¹ corresponding to coordinated pyridine and characteristic of Lewis acid sites were detected [36]. Similar spectra were obtained for many of the Ag/ZrO₂/SiO₂ catalysts. The increase in intensity of these bands with ZrO₂ loading is indicative of an increase of the concentration of the Lewis acid sites. Note that a similar trend was observed for the IR spectra recorded after desorption of pyridine at 250 °C and 350 °C. In agreement with a previous study concerning SiO₂ materials the spectra do not exhibit the presence of Brønsted acid sites because no bands located at ~1540 and ~1645 cm⁻¹ were detected [22]. However, the presence of a minor amount of Brønsted acid sites cannot be completely ruled out. The catalysts may contain a small amount of Brønsted acid sites that are too weak to protonate pyridine.

The concentrations of Lewis acid sites provided in Table 8 increase from 17.3 μmoles/g to 28.4 μmoles/g when the ZrO₂ loading increases from 1 to 10 wt.%. The results do not show a relationship between the concentration of Lewis acid sites and conversion. Conversion increases slightly from ~79% to ~86% when the concentration of Lewis acid sites increases from 17.3 to 26 μmoles/g, but further increases in the concentrations of acid sites result in decreased conversion. For Ag/ZrO₂

catalysts supported on SiO₂, MCM-41, and Zeolite Beta, an increase in conversion as the concentration of Lewis acid sites increases has been reported previously [16]. The supports were different in structure, acid strength, and the nature of the acid sites, and each of these parameters could affect conversion performance. Establishing a relationship between conversion and acidity is not straightforward. In our study the same support namely SiO₂-646 was used. Fig. 6(b) shows the evolution of butadiene selectivity as the concentration Lewis acid sites is changed. One can see that butadiene selectivity decreases from about 71% to 62% as the concentration of Lewis acid sites increases. Lower Lewis acid site concentrations are preferred to promote higher selectivity to butadiene. A similar trend was observed for 1 Ag/4ZrO₂/SiO₂ catalysts prepared from different silica materials, and similar conversion between 75 and 85% are shown in Fig. 7. Thus, these results demonstrate a direct relationship between butadiene selectivity and Lewis acid site concentration.

Initially, the decrease in butadiene selectivity with the increase of the Lewis acid site concentrations could appear surprising. Indeed, Lewis acid sites are generally accepted to be favorable to the ETB process [13,15,22,28], and one would expect butadiene selectivity to increase as the concentration of the Lewis acid sites increases. In this study, increasing the concentration of Lewis acid sites from 17.3 to 28.4 μmoles/g leads to a decrease of the acetaldehyde selectivity from 14.2% to 9.3%, thus confirming that increasing the concentration of Lewis acid sites favors the aldol condensation. In addition, the decrease of butadiene selectivity is accompanied with an increase of butene, ethylene, and DEE selectivity from 2.4 to 5.7%, 4.1 to 8.4%, and 1.3 to 2.5%, respectively. Ethylene and DEE formation result from ethanol

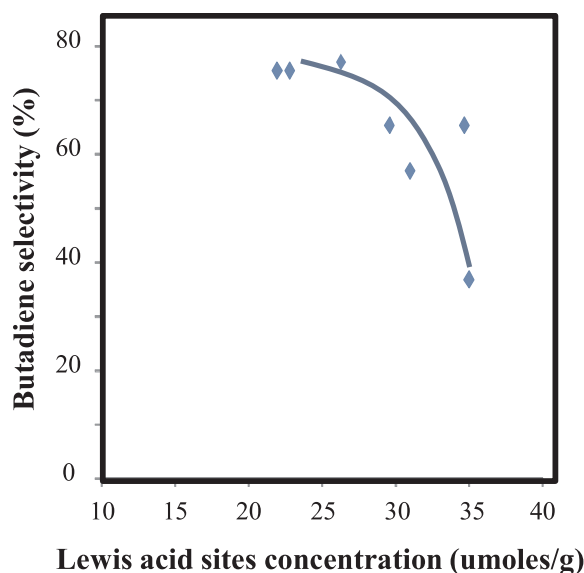


Fig. 7. Evolution of the butadiene selectivity with the Lewis acid sites concentration for 1 Ag/4ZrO₂/SiO₂ catalysts. Lewis acid sites concentration determined after pyridine desorption at 150 °C. Butadiene selectivity at 75–85% conversion.

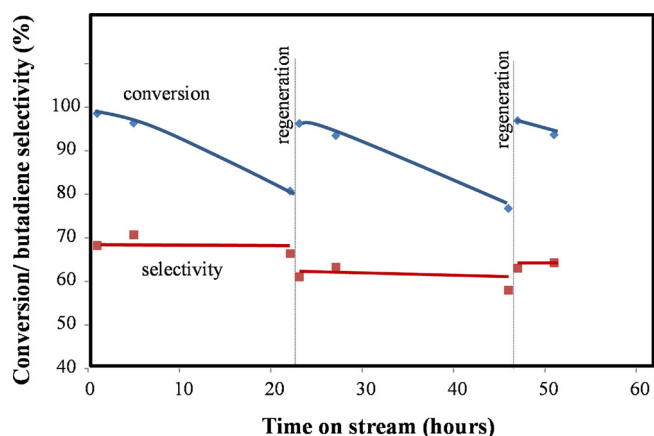


Fig. 8. Catalyst lifetime and regenerability for 1 Ag/4ZrO₂/SiO₂-SBA16. T = 325 °C, P = 1 atmosphere, WHSV = 0.23 h⁻¹, 24.3% ethanol/N₂.

dehydration over acid sites [37,38]. Butenes also could be formed from butanol dehydration over acid sites with butanol being produced from crotyl alcohol. These acid-catalyzed side-reactions can thus explain the decrease of butadiene selectivity with the increase in the concentration of acid sites. Hence, our results demonstrate that Lewis acid sites are needed to convert acetaldehyde into butadiene but that only a small concentration of Lewis acid sites is needed to avoid side-reactions catalyzed by acid sites.

4. Catalyst lifetime and regenerability

Catalyst stability has been a long-standing challenge for ETB and catalyst deactivation due to coking is a major issue [39]. Although very limited research has been done, one study has proposed the use of a process initiator (i.e., hydrogen peroxide) as a potential solution to limit coking [40]. However, the use of a process initiator might not be applicable to industrial processes. The stability and regenerability results obtained for 1 Ag/4ZrO₂/SiO₂-SBA16 are shown in Fig. 8. Conversion decreases from 98% at a 5 h TOS to 81% after 22 h TOS. However, the butadiene selectivity remains fairly stable at approximately 70%. A similar trend was observed for Ag/ZrO₂/Beta catalysts,

and the loss of activity was attributed to gradual poisoning of the active sites by coke deposits [13]. In our study, deactivation probably the result of coking from heavy compounds because aromatic liquid products (e.g. xylene and other branched benzenes) were detected when a notable reduction in conversion was observed. Two successful regeneration cycles were conducted under flowing 5% O₂/He for 4 to 5 h at 500 °C followed by a reduction treatment at 325 °C under 10% H₂/N₂ for 1 h. Indeed, after the oxidation/reduction treatment, the catalyst regains its initial conversion. This highlights the effectiveness of this oxidative treatment for complete regeneration of the Ag/ZrO₂/SiO₂ system.

Additional stability measurements were performed in the presence of H₂ co-feed. Results obtained for 4 Ag/4ZrO₂/SiO₂-646 and 2Ir/4ZrO₂/SiO₂-646 are shown in Fig. 9. In the presence of H₂, catalyst stability improved as it decreased only from ~98 to 94% for 2Ir/4ZrO₂/SiO₂-646 and from 88% to 83% for 4 Ag/4ZrO₂/SiO₂-646. In comparison, in the absence of H₂, conversion decreases from 96% to 85% and from 92% to 78% for 2Ir/4ZrO₂/SiO₂-646 and 4 Ag/4ZrO₂/SiO₂-646, respectively. Aromatic species precursors of coke are likely formed via cyclization of olefins, which involves dehydrogenation. Addition of H₂ to the feed gas favors hydrogenation reactions and can impede oligomerization and dehydrogenation reactions, thereby leading to the formation of aromatics. This could explain the improved catalyst stability that is observed in the presence of H₂.

5. Conclusions

Various Ag/ZrO₂/SiO₂ catalysts were studied for use in single-step ETB conversion. The catalyst composition and the role of each component in the composition were examined by varying parameters such as the choice of metal promoter (i.e., Ag, Ir, or Pt), Ag loading, ZrO₂ loading, and characteristics of SiO₂ supports (e.g., acidity, surface area). Operating conditions such as space velocity and feed gas composition (e.g., pure N₂ or N₂/H₂ co-feed) also were investigated. Our study has yielded significant findings that enable better understanding of ETB reactivity over Ag/ZrO₂/SiO₂ catalysts. These findings are summarized here:

- Over Ag/ZrO₂/SiO₂ catalysts the ETB reaction follows the aldol condensation mechanism (Fig. 1). While Ag plays a major role in ethanol conversion to acetaldehyde, Lewis acid sites are responsible for the conversion of acetaldehyde to butadiene.
- Adding H₂ to the feed gas does not affect the initial conversion; however, selectivity to butadiene and butenes are impacted. While moderate changes in selectivity were found for the supported Ag catalyst, a significant decrease of butadiene selectivity and increase of butenes selectivity was observed when replacing Ag with Ir. In addition, H₂ addition to the feed improves catalyst stability.
- A total of 11 1 Ag/4ZrO₂/SiO₂ catalysts supported on different SiO₂ were tested under similar reaction conditions. Depending on the choice of SiO₂ support, drastic differences in conversion and selectivity were observed. The surface area of SiO₂ has a direct impact on conversion, which increases as the SiO₂/catalyst surface area increases because of increased Ag dispersion. Butadiene selectivity also greatly depends on the SiO₂ support. The interaction between SiO₂ and ZrO₂ differs depending on the SiO₂ support, which affects catalyst acidity and consequently butadiene selectivity. The SBA16 catalyst outperforms the other 10 SiO₂ support as evidenced by the excellent performance attained by a 1 Ag/4ZrO₂/SiO₂-SBA16 catalyst, which exhibited a ~70% butadiene yield and ~90% yield of total olefins at 99% ethanol conversion.
- By independently varying the Ag and the ZrO₂ loadings, we found that the optimal composition for a silica gel supported catalyst is 4 wt.% Ag and 4 wt.% ZrO₂.
- The direct relationship between butadiene selectivity and concentration of Lewis acid sites was demonstrated. Butadiene

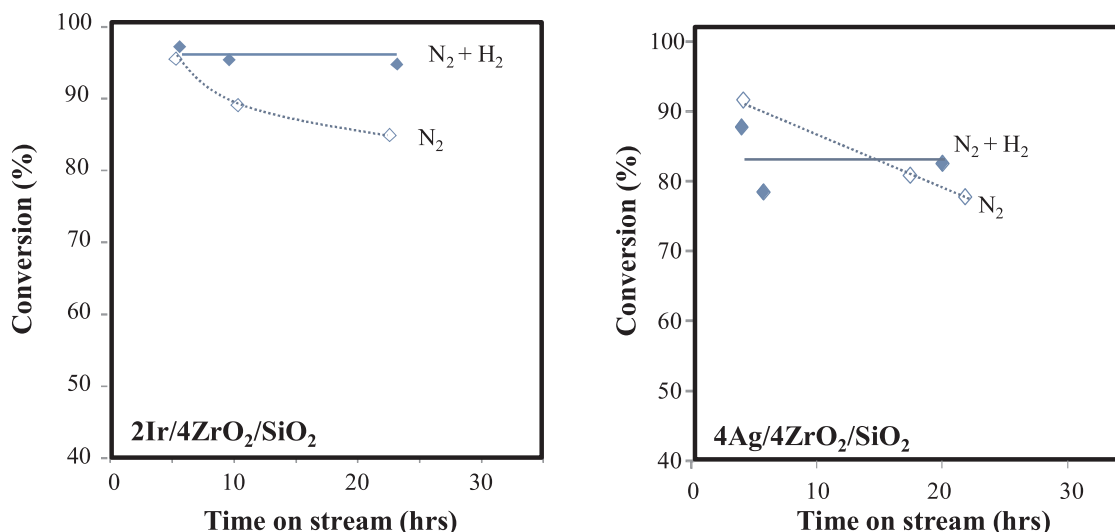


Fig. 9. Evolution of the conversion as a function of the time on stream for 2Ir/4ZrO₂/SiO₂ and 4Ag/4ZrO₂/SiO₂-646. T = 325 °C, P = 1 atmosphere, WHSV = 0.23 h⁻¹, 24.3% ethanol in N₂ or N₂/H₂ mixture.

selectivity decreases as the concentration of Lewis acid sites increases. Lewis acid sites are needed to convert acetaldehyde into butadiene but only a small concentration (≤ 17.3 $\mu\text{moles/g}$ in our study for 4Ag/ZrO₂/SiO₂ catalysts) is needed to avoid acid-catalyzed side reactions such as ethanol dehydration to ethylene and DEE.

- Our study of catalyst stability found that conversion decreases over time as a result of coking. Efficient catalyst regenerability was successfully demonstrated for multiple cycles.

Future work will focus on other promoted SBA-16 catalysts. In this work deeper characterization studies coupled with reactivity measurements will be undertaken.

Acknowledgments

This work was financially supported by the U.S. Department of Energy (DOE) Bioenergy Technologies Office and performed at the Pacific Northwest National Laboratory (PNNL). PNNL is a multi-program national laboratory operated for DOE by Battelle Memorial Institute. Catalyst characterization equipment use was granted by a user proposal at the William R. Wiley Environmental Molecular Sciences Laboratory, which is a national scientific user facility sponsored by the DOE Office of Biological and Environmental Research and located at PNNL. The authors want to thanks JSC Karpov Chemical Plant for providing two silica gels KSKG-GOST 3956-76 and KSMG-GOST 3956-76. The authors greatly acknowledge Marie Swita for her help with the gas chromatography-mass spectrometry analysis.

The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

References

- [1] E.V. Makshina, M. Dusselier, W. Janssens, J. Degreve, P.A. Jacobs, B.F. Sels, Review of old chemistry and new catalytic advances in the on-purpose synthesis of butadiene, *Chem. Soc. Rev.* 43 (2014) 7917–7953.
- [2] J.S. Plotkin, *The Continuing Quest for Butadiene*, American Chemical Society, 2016.
- [3] W.C. White, Butadiene production process overview, *Chem. Biol. Interact.* 166 (2007) 10–14.
- [4] M.D. Jones, Catalytic transformation of ethanol into 1,3-butadiene, *Chem. Central J.* 8 (2014) 53.
- [5] J. Sun, Y. Wang, Recent advances in catalytic conversion of ethanol to chemicals, *ACS Catal.* 4 (2014) 1078–1090.
- [6] A.D. Patel, K. Meesters, H. den Uil, E. de Jong, K. Blok, M.K. Patel, Sustainability assessment of novel chemical processes at early stage: application to biobased processes, *Energy Environ. Sci.* 5 (2012) 8430–8444.
- [7] A.D. Patel, K. Meesters, H. den Uil, E. de Jong, E. Worrell, M.K. Patel, Early-stage comparative sustainability assessment of new bio-based processes, *ChemSusChem* 6 (2013) 1724–1736.
- [8] C. Angelici, B.M. Weckhuysen, P.C.A. Bruijninx, Chemocatalytic conversion of ethanol into butadiene and other bulk chemicals, *ChemSusChem* 6 (2013) 1595–1614.
- [9] B.B. Corson, H.E. Jones, C.E. Welling, J.A. Hinckley, E.E. Stahly, Butadiene from ethyl alcohol - catalysis in the one-step and 2-step processes, *Ind. Eng. Chem.* (1950) 42.
- [10] Q. Zhu, B. Wang, T. Tan, Conversion of ethanol and acetaldehyde to butadiene over MgO–SiO₂ catalysts: effect of reaction parameters and interaction between MgO and SiO₂ on catalytic performance, *ACS Sustain. Chem. Eng.* 5 (2017) 722–733.
- [11] E.V. Makshina, W. Janssens, B.F. Sels, P.A. Jacobs, Catalytic study of the conversion of ethanol into 1,3-butadiene, *Catal. Today* (2012) 198.
- [12] S.K. Bhattacharyya, N.D. Ganguly, One-step catalytic conversion of ethanol to butadiene in the fixed bed. II BINARY- AND TERNARY-OXIDE CATALYSTS, *J. Appl. Chem.* 12 (1962) 105–110.
- [13] V.L. Sushkevich, D. Palagin, I.I. Ivanova, With Open arms: Open sites of ZrBEA zeolite facilitate selective synthesis of butadiene from ethanol, *ACS Catal.* 5 (2015) 4833–4836.
- [14] V.L. Sushkevich, I.I. Ivanova, Ag-promoted ZrBEA zeolites obtained by Post-synthetic modification for conversion of ethanol to butadiene, *ChemSusChem* 9 (2016) 2216–2225.
- [15] T. De Baerdemaeker, M. Feyen, U. Müller, B. Yilmaz, F.-S. Xiao, W. Zhang, T. Yokoi, X. Bao, H. Gies, D.E. De Vos, Bimetallic Zn and Hf on silica catalysts for the conversion of ethanol to 1,3-butadiene, *ACS Catal.* 5 (2015) 3393–3397.
- [16] V.L. Sushkevich, I.I. Ivanova, E. Taarning, Ethanol conversion into butadiene over Zr-containing molecular sieves doped with silver, *Green Chem.* 17 (2015) 2552–2559.
- [17] V.L. Sushkevich, I.I. Ivanova, V.V. Ordonsky, E. Taarning, Design of a metal-promoted oxide catalyst for the selective synthesis of butadiene from ethanol, *ChemSusChem* 7 (2014) 2527–2536.
- [18] C.A. Emeis, Determination of integrated molar extinction coefficients for infrared absorption bands of pyridine adsorbed on solid acid catalysts, *J. Catal.* 141 (1993) 347–354.
- [19] G. Egloff, G. Hulla, Conversion of oxygen derivatives of hydrocarbons into butadiene, *Chem. Rev.* 36 (1945) 63–141.
- [20] H.E. Jones, E.E. Stahly, B.B. Corson, Butadiene from ethanol. Reaction mechanism, *J. Am. Chemical Society* 71 (1949) 1822–1828.
- [21] P. Müller, S.-C. Wang, S.P. Burt, I. Hermans, Influence of metal doping on the Lewis Acid catalyzed production of butadiene from ethanol studied by using modulated operando diffuse reflectance infrared fourier transform spectroscopy and mass spectrometry, *ChemCatChem* 9 (2017) 3572–3582.
- [22] W. Janssens, E.V. Makshina, P. Vanelder, F. De Clippel, K. Houthoofd, S. Kerkhofs, J.A. Martens, P.A. Jacobs, B.F. Sels, Cover picture: ternary Ag/MgO–SiO₂ catalysts for the conversion of ethanol into butadiene (*ChemSusChem* 6/2015), *ChemSusChem* 8 (2015) 911–911.

- [23] V. Gruver, A. Sun, J.J. Fripiat, Catalytic properties of aluminated sepiolite in ethanol conversion, *Catal. Lett.* (1995) 34.
- [24] V.L. Sushkevich, I.I. Ivanova, Mechanistic study of ethanol conversion into butadiene over silver promoted zirconia catalysts, *Appl. Catal. B: Environ.* 215 (2017) 36–49.
- [25] V.L. Sushkevich, I.I. Ivanova, E. Taarning, Mechanistic study of ethanol dehydrogenation over silica-supported silver, *ChemCatChem* 5 (2013) 2367–2373.
- [26] V.L. Sushkevich, I.I. Ivanova, S. Tolborg, E. Taarning, Meerwein–Ponndorf–Verley–Oppenauer reaction of crotonaldehyde with ethanol over Zr-containing catalysts, *J. Catal.* 316 (2014) 121–129.
- [27] H.-J. Chae, T.-W. Kim, Y.-K. Moon, H.-K. Kim, K.-E. Jeong, C.-U. Kim, S.-Y. Jeong, Butadiene production from bioethanol and acetaldehyde over tantalum oxide-supported ordered mesoporous silica catalysts, *Appl. Catal. B-Environ.* (2014) 150.
- [28] M.D. Jones, C.G. Keir, C. Di Iulio, R.A.M. Robertson, C.V. Williams, D.C. Apperley, Investigations into the conversion of ethanol into 1,3-butadiene, *Catal. Sci. Technol.* (2011) 1.
- [29] W. Dai, S. Zhang, Z. Yu, T. Yan, G. Wu, N. Guan, L. Li, Zeolite structural confinement effects enhance one-pot catalytic conversion of ethanol to butadiene, *ACS Catal.* 7 (2017) 3703–3706.
- [30] D.E. Resasco, Dehydrogenation – Heterogeneous, *Encyclopedia of Catalysis*, John Wiley & Sons, Inc., 2002.
- [31] V.L. Dagle, R. Dagle, L. Kovarik, A. Genc, Y.-G. Wang, M. Bowden, H. Wan, M. Flake, V.-A. Glezakou, D.L. King, R. Rousseau, Steam reforming of hydrocarbons from biomass-derived syngas over MgAl₂O₄-supported transition metals and bi-metallic IrNi catalysts, *Appl. Catal. B: Environ.* 184 (2016) 142–152.
- [32] D. Mei, V.-A. Glezakou, V. Lebarbier, L. Kovarik, H. Wan, K.O. Albrecht, M. Gerber, R. Rousseau, R.A. Dagle, Highly active and stable MgAl₂O₄-supported Rh and Ir catalysts for methane steam reforming: a combined experimental and theoretical study, *J. Catal.* 316 (2014) 11–23.
- [33] D. Mei, V.M. Lebarbier, R. Rousseau, V.-A. Glezakou, K.O. Albrecht, L. Kovarik, M. Flake, R.A. Dagle, Comparative investigation of benzene steam reforming over spinel supported Rh and Ir catalysts, *ACS Catal.* 3 (2013) 1133–1143.
- [34] M.D. Jones, C.G. Keir, C.D. Iulio, R.A.M. Robertson, C.V. Williams, D.C. Apperley, Investigations into the conversion of ethanol into 1,3-butadiene, *Catal. Sci. Technol.* 1 (2011) 267–272.
- [35] V.V. Ordonsky, V.L. Sushkevich, I.I. Ivanova, Study of acetaldehyde condensation chemistry over magnesia and zirconia supported on silica, *J. Mol. Catal. A Chem.* 333 (2010) 85–93.
- [36] T. Onfroy, G. Clet, S. Bukallah, D. Hercules, M. Houalla, Development of the acidity of zirconia-supported niobia catalysts, *Catal. Lett.* 89 (2003) 15–19.
- [37] D. Varisli, T. Dogu, G. Dogu, Ethylene and diethyl-ether production by dehydration reaction of ethanol over different heteropolyacid catalysts, *Chem. Eng. Sci.* 62 (2007) 5349–5352.
- [38] K.A. Tarach, J. Tekla, W. Makowski, U. Filek, K. Mlekodaj, V. Girman, M. Choi, K. Gora-Marek, Catalytic dehydration of ethanol over hierarchical ZSM-5 zeolites: studies of their acidity and porosity properties, *Catal. Sci. Technol.* 6 (2016) 3568–3584.
- [39] G.O. Ezinkwo, V.P. Tretyakov, A. Aliyu, A.M. Ilolov, Fundamental issues of catalytic conversion of bio-ethanol into butadiene, *Chem. BioEng. Rev.* 1 (2014) 194–203.
- [40] G.O. Ezinkwo, V.F. Tretjakov, R.M. Talyshinky, A.M. Ilolov, T.A. Mutombo, Creation of a continuous process for bio-ethanol to butadiene conversion via the use of a process initiator, *Catal. Commun.* (2014) 43.